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A Review of the Potential  
for Obtaining  
Natural Gas from Sub-surface Hydrate Formations

by

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Table of Contents

|  |    |
|--|----|
| Introduction . . . . .                                 | 1  |
| Nature of Gas Hydrate. . . . .                         | 4  |
| Thermodynamic Properties. . . . .                      | 5  |
| Theoretical Model . . . . .                            | 7  |
| Composition of Gas Hydrates . . . . .                  | 8  |
| Hydrates in Subsurface Environments. . . . .           | 10 |
| Hydrates in Porous Rock . . . . .                      | 10 |
| Hydrates in Marine Sediments. . . . .                  | 12 |
| Depth of Hydrate Formations . . . . .                  | 19 |
| Hydrate Dissociation . . . . .                         | 24 |
| Energy Required to Dissociate Hydrates . . . . .       | 26 |
| Summary and Implications for Future Research . . . . . | 37 |
| Bibliography of Gas Hydrates . . . . .                 | 40 |

## Natural Gas From Sub-surface Hydrate Formations

Gas hydrates are crystalline, ice-like compounds composed of water and natural gas. Until recently their importance to the petroleum and natural gas industries was attributable to the formation of solid gas hydrates in gas pipelines (Hammerschmidt, 1931). Most studies of hydrates during the last half century have concentrated on experimental measurement and theoretical prediction of the pressure, temperature and composition conditions of hydrate formation (Katz et al, 1959; Byk and Fomina, 1968; Parrish and Prausnitz, 1972). The discovery of natural gas and oil in colder climatic regions such as Alaska, Canada's Northwest Territory, and Russian Siberia, has renewed interest in gas hydrates because of the possibility that such hydrates contain vast quantities of natural gas. Reports of naturally occurring gas hydrates in these regions have been made in several instances (Bily and Dick, 1973; Chersky and Makogon, 1970; Sapir, 1973) and studies by Katz and others (Katz, 1971; Katz, 1972; Holder et al, 1976) indicate that hydrates may have formed in some of the oil reservoirs in the Prudhoe Bay Area. Simultaneously, work by Stoll, Ewing and Bryan (Stoll, 1971; Bryan, 1974; Tucholke, Bryan and Ewing, 1977) has shown that large hydrate fields may exist under the ocean.

For those instances where hydrates exist in conjunction with oil or free gas, the presence of hydrates is important, not only as a potential source of free gas, but also in the way they affect the producibility of the petroleum or natural gas reservoir. Hydrates will block reservoir pores and will selectively remove high vapor pressure components such as methane thus reducing the driving force for production of any such reservoir (Verma, et al, 1975; Holder, et al, 1976).

Thus the existence of hydrates in the earth has diverse implications. Recent estimates have indicated that as much as  $10^{18}$  cubic meters of natural gas may exist in in situ hydrates (Milton, 1976, Makogon, 1974). This quantity is six times greater than the total amount of methane previously estimated to exist in the combined lithosphere and hydrosphere. It is five orders of magnitude greater than the U.S. Geological Survey's estimate of the world's proven reserves of natural gas. While there is no certainty that hydrated gas can be produced economically, the potential of this resource clearly demands evaluation.

The present review examines the current body of knowledge pertaining to recovery of natural gas from gas hydrates in the earth. It summarizes literature describing 1) the structure and physical properties of hydrates, 2) the thermodynamic properties of hydrates, and 3) the indications

of hydrate formation within the earth. In the final section, areas in which future research is needed are identified.

In order to evaluate the potential for recovering gas from naturally occurring hydrates, the following information is needed.

- where hydrates exist
- in what purity do hydrate fields exist
- in what type of media do hydrates exist
- under what pressure and temperature conditions  
can hydrates be found
- what methods and how much energy is needed to  
dissociate hydrates
- how much gas will be recovered per mole of  
hydrate decomposed

Each of these questions is addressed in this review.

## NATURE OF GAS HYDRATE

Gas hydrates have been studied extensively since their discovery by Faraday in 1811. These studies revealed that hydrates were non-stoichiometric compounds and that the number of gas molecules per water molecule in the hydrate phase depended upon the conditions at which they were formed. Much of the early work on hydrates has been summarized in works by Byk and Fomina (1968) and by Katz (1959).

Two structures of clathrate hydrates called structure I and structure II are known to form from mixtures of water and light gases. Each of these structures has two approximately spherical cavities or cages of different diameter as shown in Table 1. Not all of the cavities need be occupied by gas molecules to produce a stable hydrate, but a completely unoccupied lattice phase is metastable and does not exist. The structure which forms from a given gas is strongly dependent upon the molecular size of the gas molecule with structure I generally forming from smaller molecules such as methane and ethane and structure II generally forming from larger molecules, such as propane and butane. For gas mixtures the equilibrium hydrate structure depends upon pressure, temperature, and composition. In fact, a given gas mixture may be in equilibrium with both structures at certain specific temperatures (Holder 1976).

Table I: Lattice Properties of Structure I and Structure II Hydrates

|                                     | <u>Structure</u><br><u>I</u> | <u>Structure</u><br><u>II</u> |
|-------------------------------------|------------------------------|-------------------------------|
| Number of Large Cavities/Unit Cell  | 6                            | 16                            |
| Number of Small Cavities/Unit Cell  | 2                            | 8                             |
| Number of Water Molecules/Unit Cell | 46                           | 136                           |
| Large Cavity Diameter, A            | 8.60                         | 9.46                          |
| Small Cavity Diameter, A            | 7.88                         | 7.82                          |

#### Thermodynamic Properties

Studies of hydrate equilibria especially the extensive studies of Katz and co-workers (Katz et al. 1949; Carson and Katz 1942; Noaker and Katz 1954) focused on the equilibrium P-T conditions of hydrate formation from binary mixtures of a hydrocarbon gas and water. These studies, therefore, determined the resulting three phase vapor-water rich liquid-hydrate equilibrium loci, which for a binary mixture must be univariant according to Gibbs' phase rule.

Figure 1 shows the phase diagram for methane-ethane-water hydrate forming mixtures. A gas of any indicated composition will form hydrates at pressure-temperature points above the corresponding curve. Below the curve, hydrates will decompose; high pressures and low temperatures favor hydrate formation.

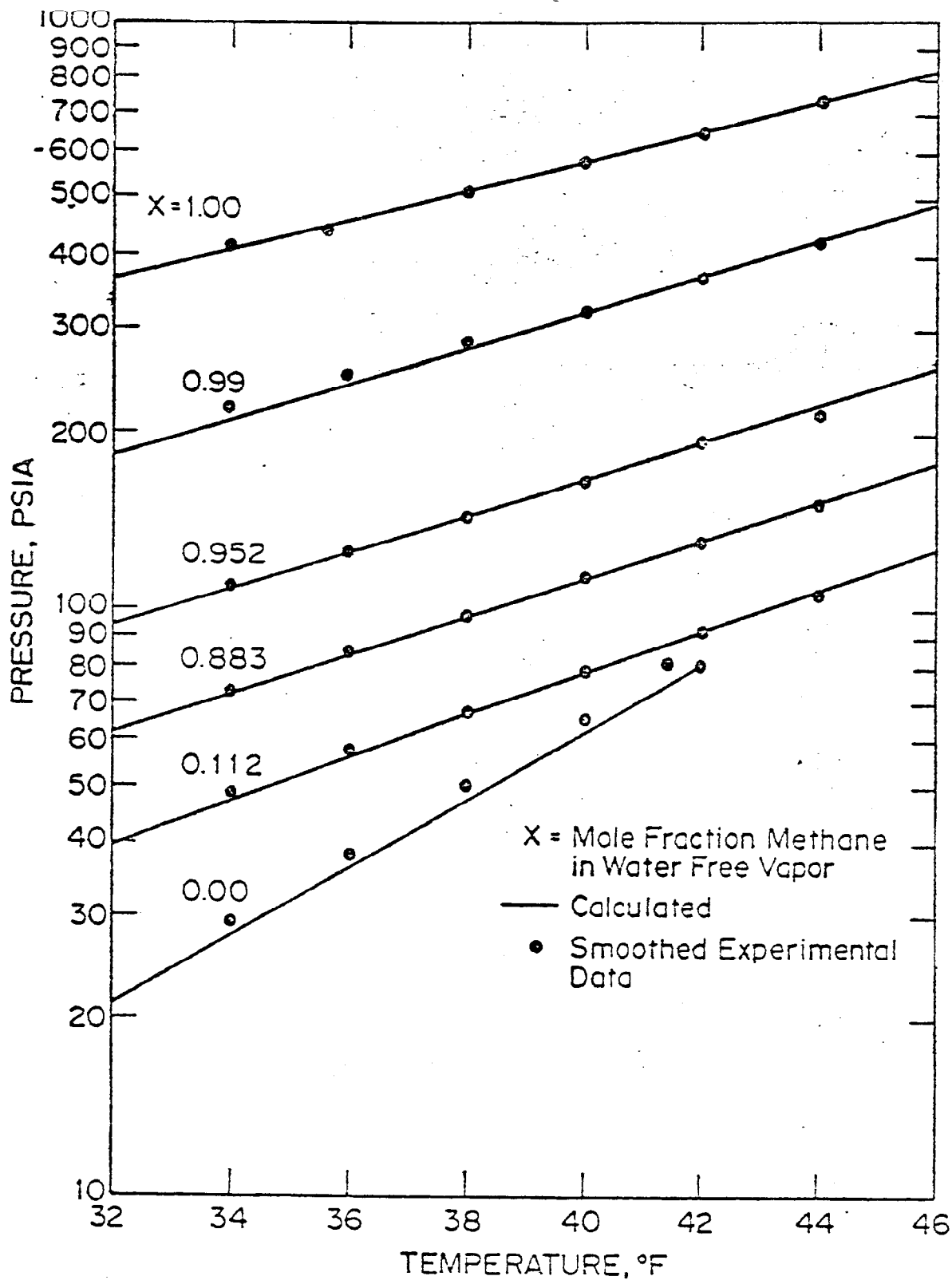


Figure 1 : DISSOCIATION PRESSURES OF METHANE-ETHANE HYDRATES  
(Holder, 1976)



The enthalpy of formation of gas hydrates, from water and free gas can be approximated by

$$\Delta H = zRT^2 \frac{d \ln p}{dT} \quad (1)$$

where R is the gas constant and z is the compressibility factor. The derivative  $d \ln p / dT$  is the slope of the semi-logarithmic P-T curve as shown on Figure 1. The calculation of this enthalpy is important because it gives the energy required to dissociate the hydrates. This energy, depending upon temperature and composition ranges from 10 to 30 k calories per mole of hydrated gas.

#### Theoretical Model

The x-ray studies of Stackleberg and co-workers (Stackleberg and Müller 1954) produced the previously mentioned structural models for hydrates and allowed the development of a statistical thermodynamic model for describing the molecular interactions in hydrate crystals. The basic model, developed by van der Waals (1959) enabled the prediction of hydrate dissociation pressures of any mixture of hydrate forming gases. His model assumed that no two gas molecules occupy the same lattice cavity, and that a gas molecule interacts solely with the lattice water molecules nearest to it. The governing equation produced by this model related the chemical potential,  $\mu_H$ , of the water in the reference lattice state (0% occupancy),  $\mu_B$ , by the following

expression:

$$\mu_H = \mu_p + kT \sum_{j=1}^2 v_j \ln (1 - \sum_i \theta_{ij}) \quad (2)$$

where  $\theta_{ij}$  is the fraction of cavities occupied by gas species  $i$ ;  $v_j$  are the ratio of cavities to water molecules for two differently sized cavities. This model not only allowed for the possibility of varying hydrate numbers (ratio of water molecules to gas molecules), but required that this number be temperature dependent. The summation,  $\sum_i$ , is over the number of gas types,  $i$ , present.

This model with some modifications can predict hydrate equilibrium with varying accuracy (Parrish and Prausnitz, 1972; Saito and Kobayashi, 1964; Holder, 1976). It serves as the basis for hydrate equilibrium calculations that are being studied at several institutions. Such predictive techniques are invaluable aids in determining the conditions at which hydrates may form within the earth.

#### Composition of Gas Hydrates

The hydrates which form in the earth are likely to be structure I hydrate if only  $\text{CH}_4$  is present, or mixtures of structure I and structure II if any propane or heavier components are present (Verma, 1974). Structure I has one potentially gas containing cavity for every  $5 \frac{3}{4}$  water molecule and structure II has one cavity for every  $5 \frac{2}{3}$  water molecule. Thus, the highest concentration of gas in the hydrate phase which is possible is

$$\text{Percent Gas} = \frac{1*}{1 + 5 \cdot 2/3} (100) = 15\%$$

In practice, structure I hydrate will contain 13 to almost 15 percent methane when in equilibrium with a pure methane gas. Table 2 shows the composition of the hydrate that would be in equilibrium with a natural gas containing 97% methane, 2% ethane, and 1% propane. These compositions are calculated and may be somewhat in error, but the total percent gas in the hydrate phase should be close. Note that propane is enriched relative to methane in these hydrates. Thus a natural gas will tend to have its propane removed from the gas phase in preference to methane if hydrates form.

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Table 2: Calculated Composition of Structure II Hydrate in Equilibrium with a Natural Gas Containing 97% CH<sub>4</sub>, 2% C<sub>2</sub>H<sub>6</sub> and 1% C<sub>3</sub>H<sub>8</sub>. (Holder, 1976) Formation pressures are also given.

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| Temp. (°R) | Press. (psia) | Composition in Hydrate |                               |                               |                  |
|------------|---------------|------------------------|-------------------------------|-------------------------------|------------------|
|            |               | CH <sub>4</sub>        | C <sub>2</sub> H <sub>6</sub> | C <sub>3</sub> H <sub>8</sub> | H <sub>2</sub> O |
| 500        | 324           | 8.2                    | 0.2                           | 4.1                           | 87.5             |
| 510        | 645           | 9.9                    | 0.2                           | 3.5                           | 86.4             |
| 520        | 1417          | 11.0                   | 0.2                           | 2.9                           | 85.9             |
| 530        | 3910          | 12.3                   | 0.2                           | 2.0                           | 85.5             |
| 540        | 7895          | 12.7                   | 0.2                           | 1.8                           | 85.3             |

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## HYDRATES IN SUB-SURFACE ENVIRONMENTS

In recent years there has been a great deal of interest in the existence of natural gas in hydrate form because of the mounting evidence that vast quantities of hydrates may exist, not only beneath permafrost, but also in oceanic sediments. In the oceans, a large portion of the near-bottom marine sediments is suitable for the formation of hydrates. Moreover, in continental regions, large percentages of several land masses, including 75% of Alaska, have pressure-temperature conditions which favor the formation of hydrates (Makogon, 1974). If free gas and water are in contact in these regions hydrates must certainly exist.

Research on in situ hydrate formation has been proceeding, primarily in the Soviet Union, for over thirty years. Not until the late 1960's (Makogon, 1974) however, was the first report of in situ hydrates made.

### Hydrates in Porous Rock

Experimental studies aimed at understanding the conditions for hydrate formation within porous rock were carried out in the Soviet Union (Makogon, 1966; Makogon and Skhahakho, 1972). Using quartz sandstone as the experimental medium, hydrates were formed under carefully controlled conditions. These investigations found that the following factors influenced hydrate forming conditions:

- the degree of moisture saturation of the rock
- the gas-water contact area
- the capillary radii of the pores

Significantly, the capillary effect of the porous rock causes the vapor pressure of the water to decrease and consequently causes the required hydrate forming pressure,  $P$  (at a given temperature) to increase.

These experiments also demonstrated that the electrical resistivity of hydrates is much lower than the resistivity of the hydrate free core. A knowledge of such phenomena is important in exploratory efforts aimed at determining whether hydrates exist in the earth.

Occurrences of continental hydrates are found primarily in regions of thick permafrost, where the temperature, at any given depth within the earth, is relatively low. Katz (1971, 1972) reported that the presence of 700 meters of permafrost in Prudhoe Bay, Alaska made conditions for hydrate formation possible at depths exceeding 1200 meters. Subsequent studies (Holder, Katz, Hand, 1976) demonstrated that a dead crude oil found at 1200 meters could have been denuded of its lighter constituents (methane, ethane, propane, butane) by the formation of hydrates. This study went on to identify the effects of hydrate formation on the producibility of a hydrate reservoir, including considerable lowering of reservoir pressures, liquid phase viscosity increases, and

pore blockage. Such effects all tend to make the exploitation of a given reservoir more difficult.

Other studies of the relationship between hydrates and free gas have been made. One hypothesis (Makogon, 1974) holds that the hydrates have formed impermeable caps above gas diffusing up from the center of the earth and therefore account for much of the concentration of the natural gas that we now use. The few discoveries of hydrate reservoirs is probably attributable to the fact that their existence has only recently been verified and detection techniques have not been developed.

The presence of a hydrate cap will have two important effects. First, it will cause the reserves in a gas reservoir to be understated since the gas in hydrate form will not be included in the estimate of reserves. Secondly, the production of gas from the reservoir may result in the breakdown of the cap and in the consequent escape of the gas from the reservoir.

#### Hydrates in Marine Sediments

The possible existence of gas hydrates in marine sediments was suggested by Stoll et al. (1971) to explain unusually high seismic velocities and anomolous reflectors in gas-rich sediments on the Blake-Bahama outer ridge (Hollister, Ewing et al. 1972).

Reflectors similar to those found on the Blake-Bahama outer ridge have been reported in the North Pacific (Scholl and Croager, 1973) and in the Arctic Ocean (Gratz et al., 1976).

The Blake-Bahama outer ridge is a large topographic feature extending southeast from the Blake plateau off the coast of Florida (Figure 2). Deep seismic profiling showed that it is comprised of a vast accumulation of sediment lying on the horizontal sequence known as Horizon A (Ewing and Ewing, 1964). Since then, speculation with regard to the formation of the ridge has been based for the most part on differential deposition by ocean currents. Ewing et al. (1966) suggested that much of the sediment involved may have been eroded from the Blake plateau by the Florida current (Gulf Stream). Heezen and Hollister (1964) and Heezen et al. (1966) proposed that the ridge was built by the deep contour-following current which flows generally south along the western margin of the North Atlantic. In an attempt to explain in a somewhat more quantitative way the location, orientation, and shape of the ridge, Bryan (1970) invoked both these currents, suggesting that they interact to form a stable flow pattern which is consistent with the observed depositional pattern and therefore could have been responsible for the initiation and early growth of the ridge on a flat sea floor. In a detailed study of seismic reflection records, Markl et al. (1970) showed how this simple picture is complicated in the later stages of formation, as geostrophic effects become more dominant. The

similarity between the sedimentary structure of the ridge and that of the normal continental rise to the north was pointed out, and it was suggested that a normal continental rise would have been built against the steep Blake escarpment were it not for the deflecting influence of the Florida current.

One of the features common to the ridge and the normal rise to the north is a prominent reflecting horizon which lies approximately parallel to the sea floor at a depth corresponding to about 0.6 - 0.7 second of two-way travel time. This reflector cuts across a series of closely spaced reflectors that appear to be bedding planes (Figure 3) and thus cannot itself be a stratigraphic boundary.

Milton (1976) has suggested that the only physical surface which could transgress bedding planes and run parallel to the bottom as these anomalous reflectors do, would be an isothermal surface which itself is indicative of a phase transition such as would exist for a hydrate + gas + water equilibrium.

One of the major objectives of Leg 11 of the Deep Sea Drilling Project was to investigate the nature of this reflecting horizon. Three holes on the Blake outer ridge were drilled on DSDP Leg 11 (Hollister, Ewing et al., 1972). These drill sites are located on Figures 2 and 3. Hole 102 was drilled on the crest of the ridge at a water depth equal to an acoustic travel time of 4-1/2 seconds; holes 103 and



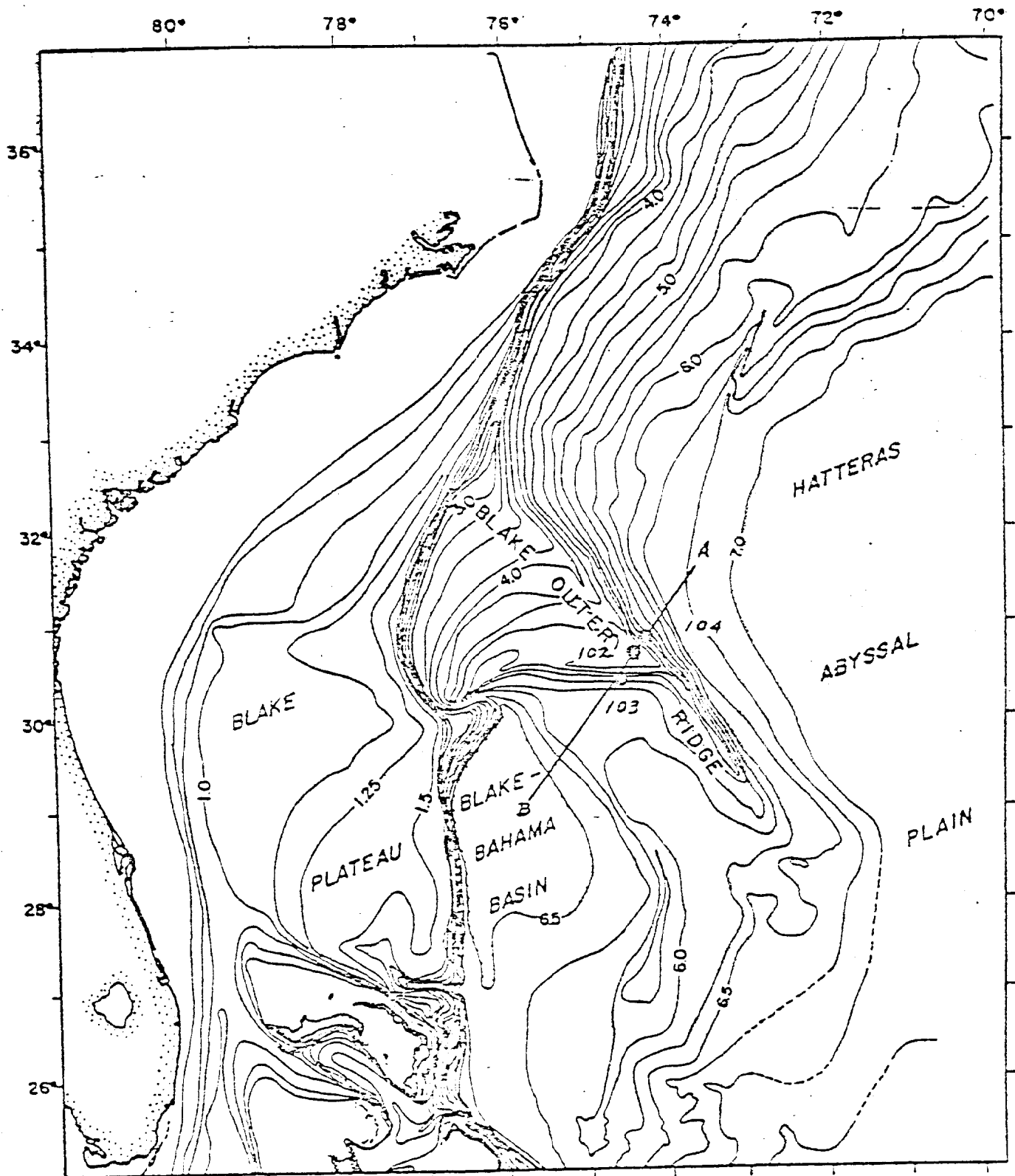


Fig. 2. Topographic contour chart of the Blake-Bahama outer ridge and environs. Line AB locates the seismic profile of Fig. 3 and the numbered points are DSDP drill sites.

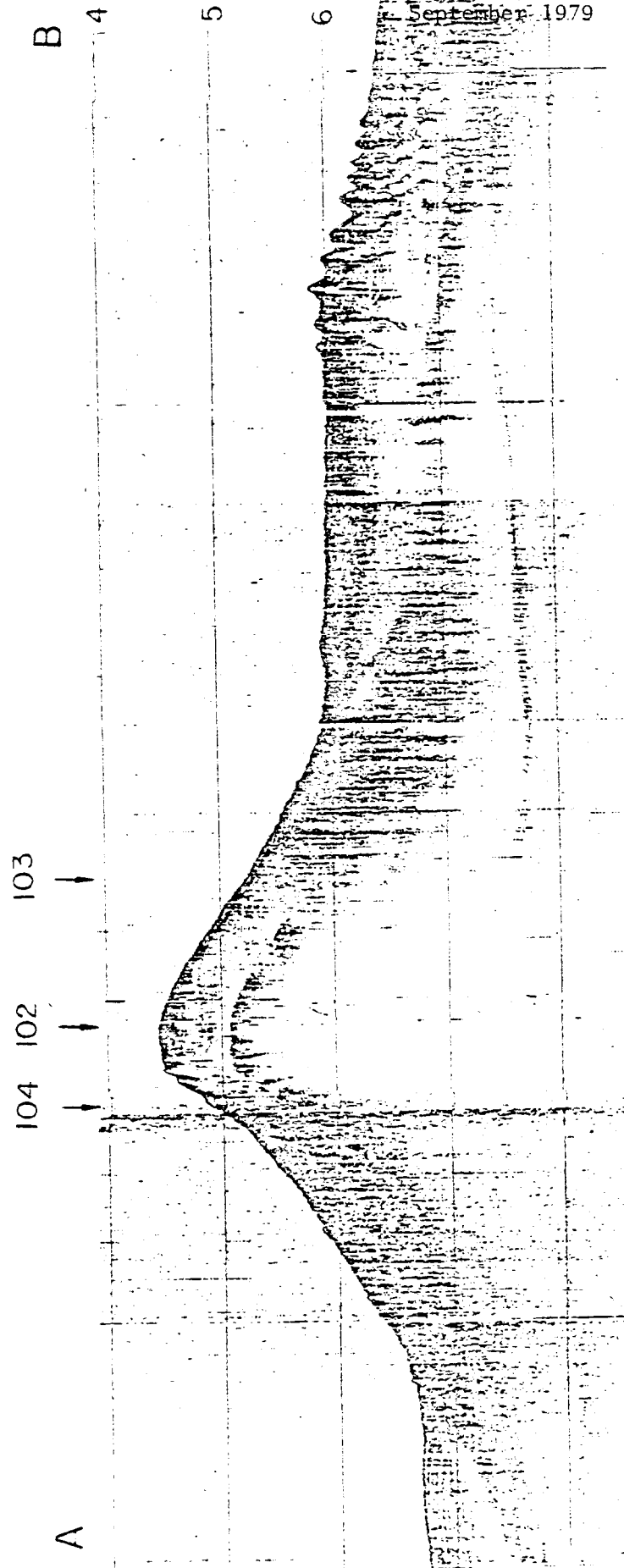


Fig. 3. Airgun profile across the Blake-Bahama outer ridge, showing major reflector about 0.6 second below bottom. Vertical scale is in seconds.

104 on the southwest and northeast flanks respectively, in a water depth equal to approximately 5 seconds travel time. The cores from all three holes consisted largely of hemipelagic mud and contained substantial quantities of gas throughout virtually the entire sediment column to a depth of 600 m below the seafloor. In many of the cores, enough gas evolved to extrude sections of core from the plastic liner, creating visible gaps. The gas was predominantly methane with traces of ethane.

The average acoustic wave velocity in the sediment based on the most obvious correlation between seismic reflections and lithologic changes was found to be over 2 km/sec, which is anomalously high when compared to velocities in sediments with similar porosity and grain size that contain no gas. More recent measurements have confirmed the high velocities originally recorded.

The occurrence of anomalously high sound velocities in sediments containing large amounts of natural gas suggests the presence of gas hydrates, and the prominent reflector is thought to be associated with the lower boundary of the hydrate zone. The reflector is present on a large part of the Blake-Bahama outer ridge and on much of the continental rise farther north.

The existence of gas hydrates in marine sediments depends on many factors such as the origin and composition of the sediment and the subbottom depth to which hydrate would be stable for the existing water depth and bottom-water

temperature. The exact combination of conditions that can produce an anomalous reflector is still a matter of conjecture since no samples of sediment containing hydrate have been recovered intact from the deep ocean sediments. Several attempts at sampling suspected deposits, using different kinds of samplers designed to maintain in situ pressure, have failed because of mechanical malfunction. The successful recovery of such a sample will go a long way towards clarifying the exact nature of the acoustic reflector caused by the presence of hydrate.

The methane content of water in contact with hydrates would be indicative of the presence of hydrate since the fugacity of methane in the water phase must equal the fugacity of methane in the hydrate and free gas phases. Measurements indicate that the methane content in sediment sea water is much less than that needed to form hydrates, but these measurements were not made in the expected hydrate zone and were also subject to considerable experimental error (Hammond, 1974). Also, there is a great deal of inconsistency in the reported measurements of the methane content of water in equilibrium with hydrate and gas (Culberson and McKetta, 1951; Enns et al., 1965; Makagon 1974, and Hemmingson, 1975). This is an area in which research would be a very valuable aid in substantiating the existence of methane hydrate.

## Depth of Hydrate

At present it is felt that the anomalous reflectors that have been observed are located at or near the subbottom depth where the temperature-pressure conditions correspond to a gas-water-hydrate equilibrium curve such as those shown in Figure 4. The impedance contrast that causes the reflections may be the result of the rigidity of a layer of hydrate-filled sediment or the result of a layer of sediment containing free gas, trapped under a hydrate clogged stratum, or a combination of both (Bryan, 1974; Tucholke et al., 1977). In any event, to calculate the depth corresponding to hydrate equilibrium, a reasonable estimate of the thermal gradient in the subbottom sediments must be made. In typical deep-water deposits of sediment, the thermal gradient is often found to be in the range of .038 to .058°C/meter (Langseth and Von Herzen, 1970); however the actual gradient at a given location depends on many factors including the magnitude of heat flow and the thermal conductivity of the sediment. Actual calculation of reflector depths requires this information.

The DSDP (Enchson, 1973) measured downhole temperatures at site 184 where the water depth is 1910 m. The thermal conductivities of the cores obtained in these sediments were also measured. Using this data, the temperature at which the anomalous reflector was found (estimated to be 600 m below the bottom) was calculated to be 49°C which is much higher than the temperature at which methane hydrates could exist. However,

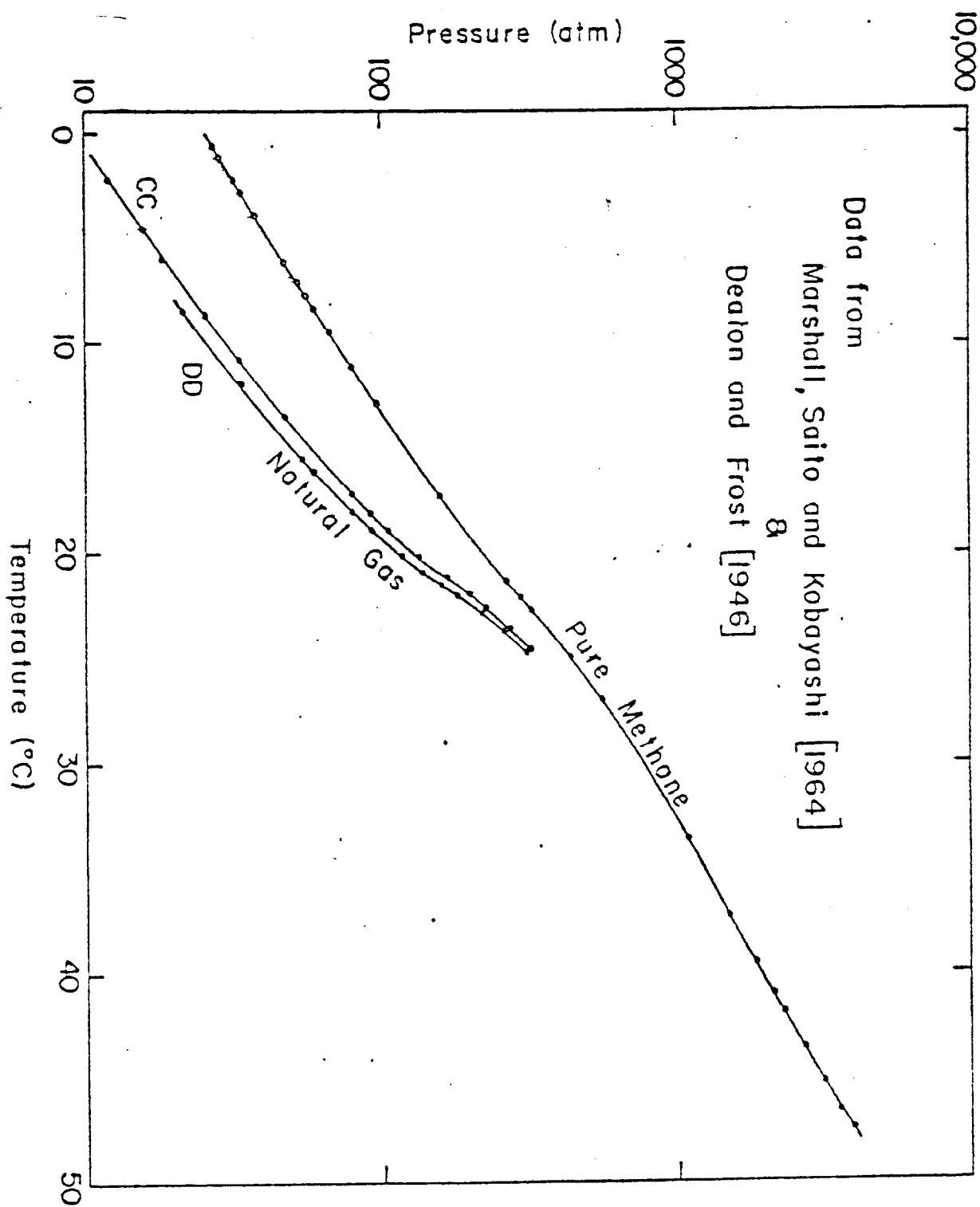


Fig. 4. Hydrate equilibrium conditions for pure methane and two samples of natural gas.

the measured thermal conductivities and temperatures could be in error and the possibility of a 24°C temperature existing at the reflector exists (Milton, 1976).

Reflectors similar to those found in the Blake-Bahama Ridge have also been found in the Benfort Sea on the continental slope of Alaska (Grantz et al., 1976). These reflectors are at more shallow depths and investigators have suggested that the hydrates may be acting as traps beneath which free gas has accumulated.

Hydrate fields beneath permafrost in Alaska are estimated to be between 200 m and 1300 m depending upon the thermal gradient and gas gravity (Katz, 1971; Katz, 1972). (In Siberia, hydrates may exist at depths of 2000 m or more.) The Alaskan estimates are based upon actual temperature profiles and an assumed hydrostatic head (0.43 psi/ft or 0.1 atm/m). If an overburdened pressure provides a greater pressure at every depth, the probable range of hydrate existence would increase. In cases such as these with measured temperature profiles, thermal conductivity still plays an important role since such temperature profiles should be consistent with the thermal conductivity of hydrates if they are present. Since hydrates appear to have a lower thermal conductivity than water or ice, the temperature gradient in the hydrate zone should be greater than the gradient above the zone.

Thus, two physical properties -- the acoustic wave velocity and the thermal conductivity -- play key roles in determining the location of potential hydrate deposits. There is virtually no information on these properties in the literature except that reported by researchers at Lamont-Doherty Geological Observatory shortly after the initial discovery of hydrates in the seafloor. This research included preliminary studies of acoustic wave velocity and thermal conductivity in pure hydrates and in sediments containing hydrates (Stoll et al., 1971; Stoll, 1974 and Stoll and Bryan, 1979). The work showed that wave velocities in sediments do increase markedly with the formation of hydrates and that thermal conductivity actually decreases (compared to water) when hydrates form. This latter observation was unexpected in view of the fact that the velocity of crystalline ice is much higher than that of water.

Another physical property that is pertinent to the location and study of in situ deposits of hydrate is electrical resistivity. Russian scientists (Makogon, 1974) have claimed that a change in electrical resistivity is one of the most significant indicators of the presence of hydrates in bore hole logs. Our only source of information on this property is one or two Russian articles which contain limited details so that more research on this effect of hydration is required.

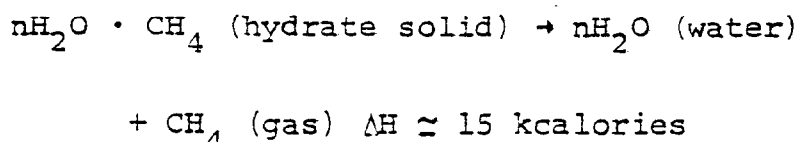
Other physical properties that are important in studies of naturally occurring hydrate formations include



shear wave velocity, compressibility under geostatic stress levels and any changes in the susceptibility of a sediment of lithification owing to the presence of variable amounts of hydrate in the interstices.

### HYDRATE DISSOCIATION

In order to dissociate\* hydrates isothermally, the energy of dissociation for the transition from hydrates to gas and water must be provided from an external source. The transition is represented by



and the energy required to dissociate the hydrates is about 15 kcal per mole of methane ( $\text{CH}_4$ ) produced. Since energy is required, simply drilling into a hydrate reservoir and relieving the pressure will not result in the rapid dissociation of hydrates since no energy is being provided. This fact has been verified in drilling operations and was predicted by Katz (1971, 1972). In this transition,  $n$  represents the number of water molecules per gas molecule in the hydrate phase. Since hydrates are non-stoichiometric compounds, this number can vary, but it will always be near 6. In practice, gases other than methane will evolve from the hydrate phase, but here all gases are represented by methane for simplicity.

The energy required to produce one mole of gas from hydrates represents about seven or eight percent of

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\*The term "dissociate" is used here to indicate a solid to gas + water transition. This transition can not be correctly called a melting or sublimation process since it is in fact a combination of these. If hydrates were dissociated at a temperature below the freezing point of water ( $0^\circ\text{C}$ ), the dissociation would represent a solid to solid + gas transition.

the heating value of the gas produced. This percentage depends upon the composition of the hydrates, but in most cases will be very near the indicated value. This means that under ideal conditions, the net gain in energy in obtaining gas from pure hydrates will exceed ninety percent of the energy value of the gas. The exact energy recovery ratio will depend upon the heat losses incurred in transferring the dissociation energy to the hydrate phase. A critical factor in the efficiency of this energy transfer will be the rate at which heat can be transferred from a thermal source, such as hot water, to the hydrate phase.

Experimental simulation of the hydrate dissociation process would allow measurement of the rates of this heat transfer. Because dissociation of hydrates involves a solid to liquid + gas transition, the heat transfer to the hydrate from adjacent thermal fluids contains some characteristics of sublimation heat transfer and some characteristics of melting heat transfer. These complicated phenomena make experimental evaluation of heat transfer process imperative.

### ENERGY REQUIRED TO DISSOCIATE HYDRATES

An estimate of the energy efficiency of hydrate production can be made (Yen, 1979). An energy balance is made over on the reservoir volume in which the hydrates have been dissociated. The boundary of the control volume is the surface at which the hydrates are dissociating.

In this model, it is assumed that steam is injected into the hydrate containing reservoir causing the hydrates to dissociate in the vicinity of the injection string bottom. An energy balance is made around the region in the reservoir where the hydrates have been dissociated assuming that this region is continuous and that its temperature can be represented by a spacially averaged temperature,  $T_A$ .

$$\Delta H_s \cdot M_s = \Delta H^* \dot{M}_G + \frac{d M_R H_R}{dt} \quad (2)$$

where  $\Delta H_s$  is the enthalpy change of the steam from the time it enters the reservoir to the time it leaves as water;  $\Delta H^*$  is the molar enthalpy change of the water and gas in the hydrate phase as it dissociates at the hydrate temperature  $T_H$  and leaves the reservoir at temperature  $T_R$ . Both of these terms include sensible heats which are much smaller than the uncertainty in the latent heat of hydrate dissociation. For the purposes of an overall energy balance, there is no advantage in making the latent heats a separate term. Note

also, that since not all dissociated gas will necessarily leave the reservoir,  $\Delta H^*$  may be larger than the molar enthalpy of hydrate dissociation.

The assumption of a constant steam injection rate,  $\dot{M}_s$ , and a constant gas production rate,  $\dot{M}_g$ , made for simplicity although these are likely to vary in the actual case. Alternatively,  $\dot{M}_s$  and  $\dot{M}_g$  could be thought of as "average" rates.

The last term in this equation gives the change in sensible heat of the reservoir from the condition when hydrates are present to the condition when no hydrates are present. Since the sensible heat of the water and gas from the dissociated hydrate is included in  $\Delta H^*$ , the last term refers only to the sensible heat of the reservoir media, for example case, porous rock. The sensible heat of the reservoir media is included separately since it depends upon porosity.

The enthalpy term  $\Delta H^*$  is related to the latent heat of dissociation, and the fraction of dissociated gas that remains in the reservoir,  $c$ , by

$$\Delta H^* = [(\Delta H_{\text{Diss}} + (Cp_s + n_H Cp_w) \Delta T)] / (1 - c) \quad (3)$$

where  $Cp_g$  is the heat capacity of the gas,  $Cp_w$  is the heat capacity of water and  $n_H$  is the number of moles of water per mole of gas in the hydrate phase. The temperature change,  $\Delta T$ , is the temperature increase in the reservoir due to steam injection. It is assumed to be uniform throughout the reservoir.

The reservoir sensible heat is given by

$$\frac{d M_{R,H}}{dt} = \frac{1-\phi}{\phi} \frac{n_H}{1-\alpha} \frac{\rho_R}{\rho_{H_2O,H}} \cdot C_{p_R} \Delta T \dot{M}_G \quad (4)$$

where  $\phi$  is the fraction of the reservoir which contains hydrates. This term can be thought of as a porosity. The terms  $\rho_R$  and  $\rho_{H_2O,H}$  are the mass density of the reservoir media and molar density of the water in the hydrate phase respectively. The heat capacity of the reservoir media,  $C_{p_R}$ , is given on a mass basis.

A comparison of sensible heat terms shows that

$$(n_H C_{p_w}) \approx 10 (C_{p_s}) \quad (5)$$

$$(n_H C_{p_w}) \approx 0.1 \frac{1-\phi}{\phi} \frac{n_H}{1-\alpha} \frac{\rho_R}{\rho_{H_2O,H}} \cdot C_{p_R}, \quad \phi \approx 0.2$$

The heat need to raise the temperature of the water is on the order of ten times that needed to raise the temperature of the gas and the heat needed to raise the temperature of the reservoir media is on the order of 10 times that needed to raise the temperature of the water ( $\phi \approx 0.2$ ). Thus the reservoir media's sensible heat capacity is much more important than that of the dissociated hydrates. However, the heat capacity of the reservoir still amounts to less than one kcalorie per mole of gas per °C. If the reservoir

hydrate fraction,  $\phi$ , was reduced to value near 0.02 then the reservoir heat capacity would approach 5 kcalories per mole of gas produced per degree of temperature rise.

Table 3: Typical Properties of Hydrates and Hydrate Reservoir

| <u>Parameter</u> | <u>Range</u> | <u>Typical</u> | <u>Units</u>                    |
|------------------|--------------|----------------|---------------------------------|
| $\phi$           | 0.1-0.8      | .2             | cc hydrate/cc reservoir         |
| $\alpha$         | 0-0.2        | .1             |                                 |
| $n_H$            | 6-7          | 6              | moles of water/mole hydrate gas |
| $\rho_R C_{pR}$  | 0.2-0.9      | 1.3            | cal/cc media/°C                 |
| $\rho_{H_2O, H}$ | 0.044-0.045  | .045           | gmole/cc                        |

The total heat balance can be written

$$\Delta H_S \cdot \dot{M}_S = (\Delta H^* + C_p^* \Delta T) \dot{M}_G \quad (6)$$

where

$$C_p^* = \frac{1-\phi}{\phi} \frac{n_H}{1-\alpha} \frac{\rho_R}{\rho_{H_2O, H}} \cdot C_{pR} \quad (7)$$

For numerical purposes here  $C_p^*$  is assigned the value 300 cal/gmole gas/°C for each mole of gas produced, although it may in fact range between 6 and 1600 cal/gmole gas/°C for the values given in Table 3. This means that for every 10°K

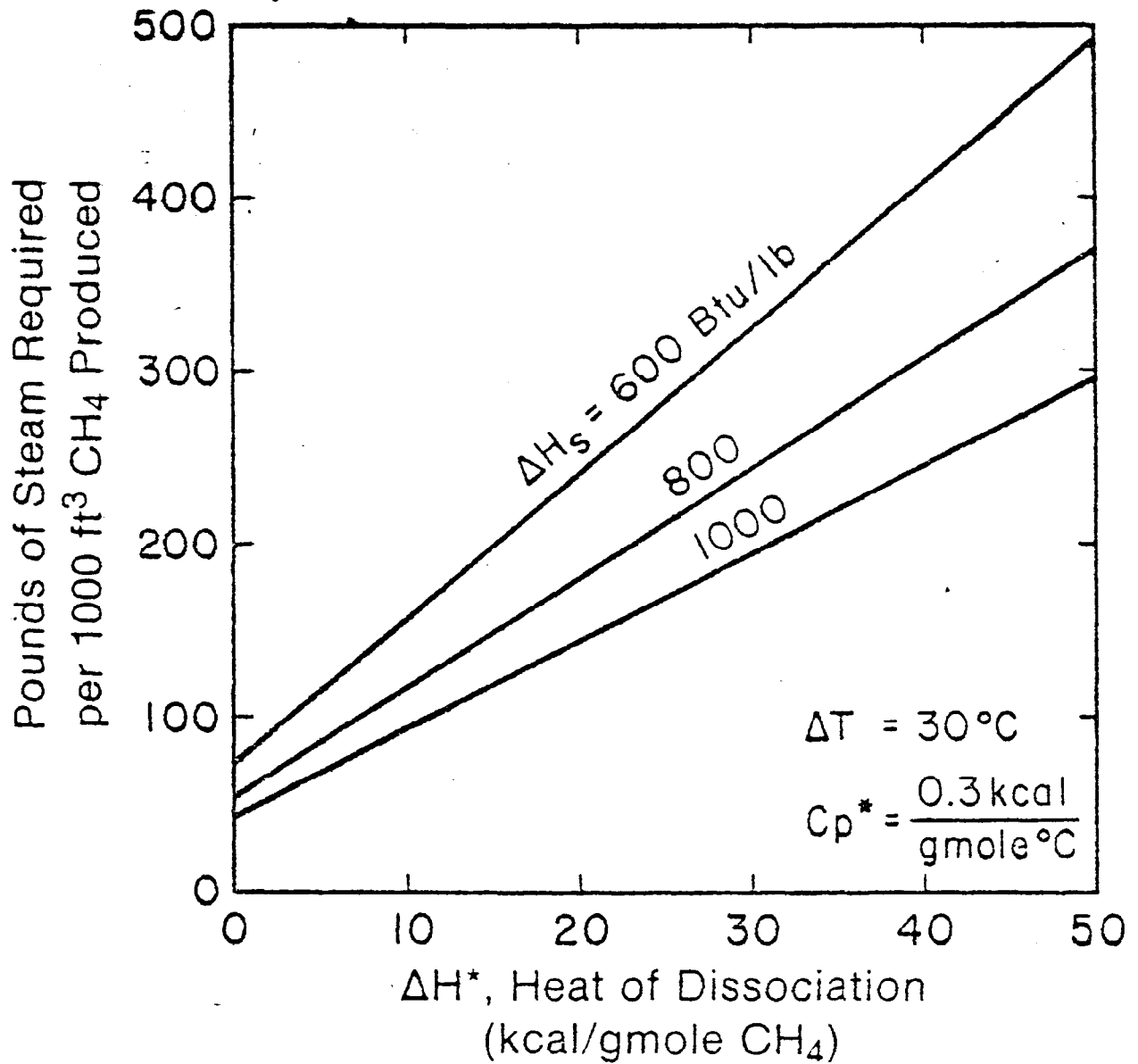


FIGURE 5: The Effect of the Latent Heat of Hydrate Dissociation on the Amount of Steam Required per Mole of Gas Produced. Case I.



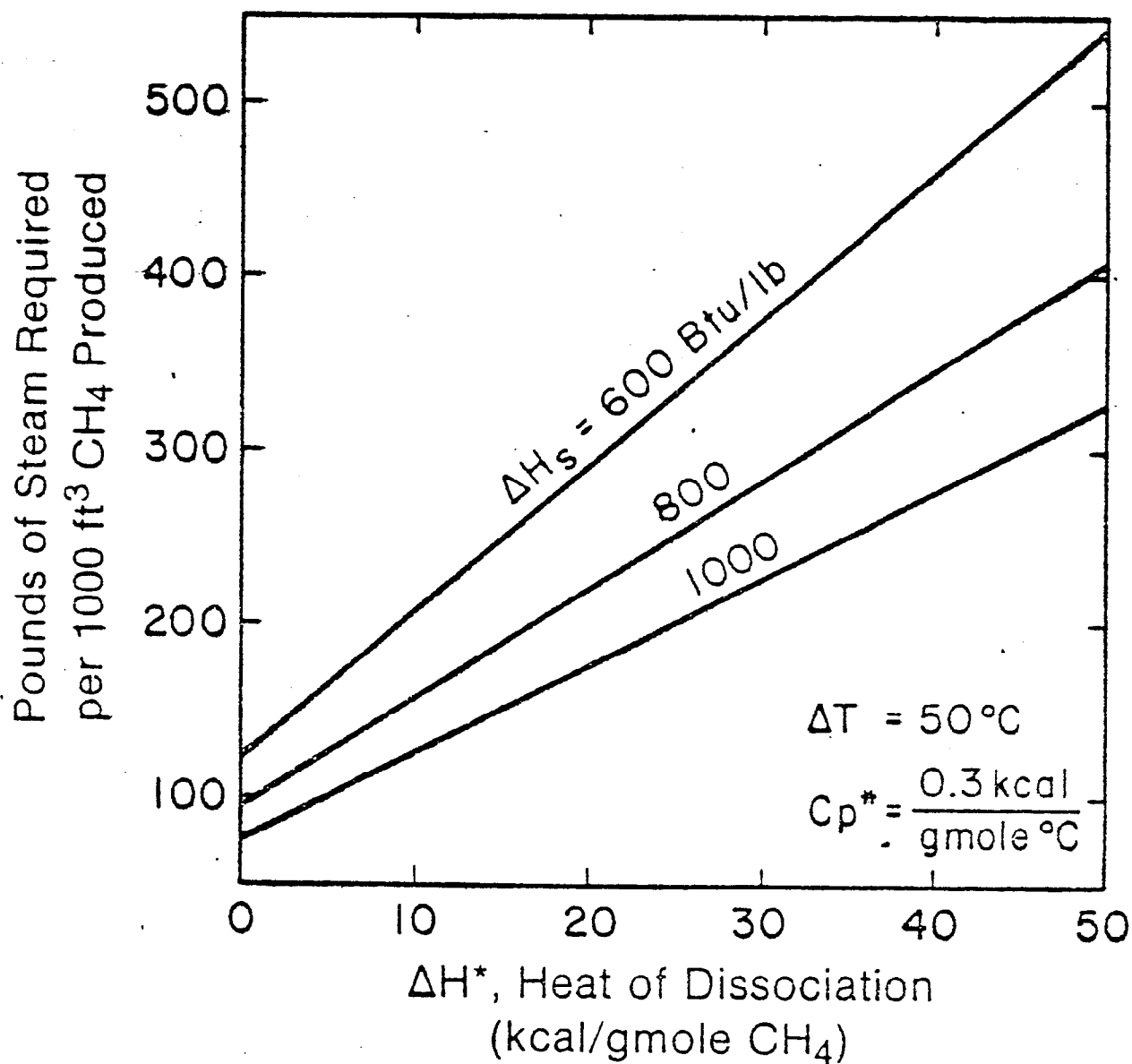


FIGURE 6: The Effect of the Latent Heat of Hydrate Dissociation on the Amount of Steam Required per Mole of Gas Produced. Case II.

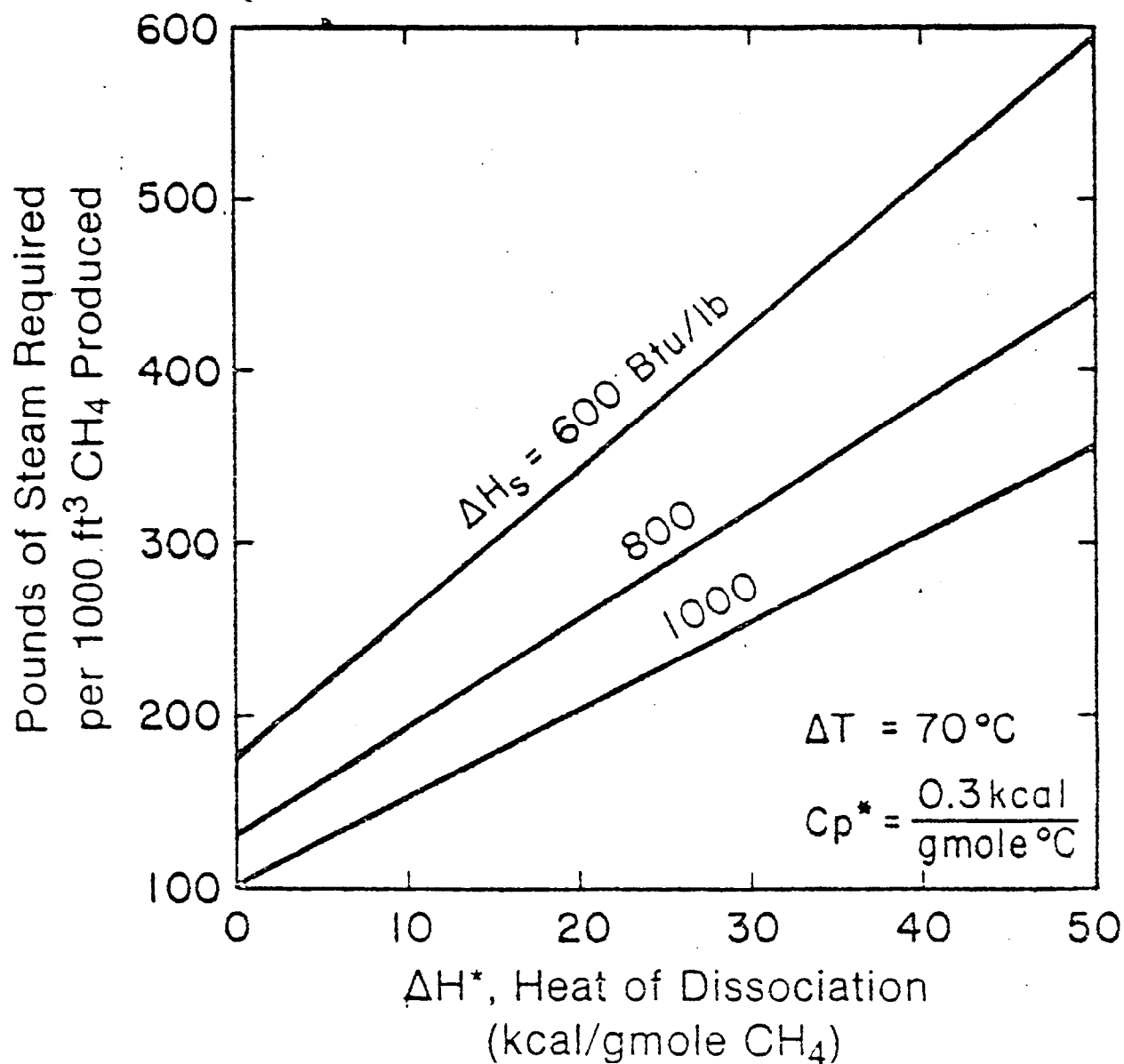


FIGURE 7: The Effect of the Latent Heat of Hydrate Dissociation on the Amount of Steam Required per Mole of Gas Produced. Case III.

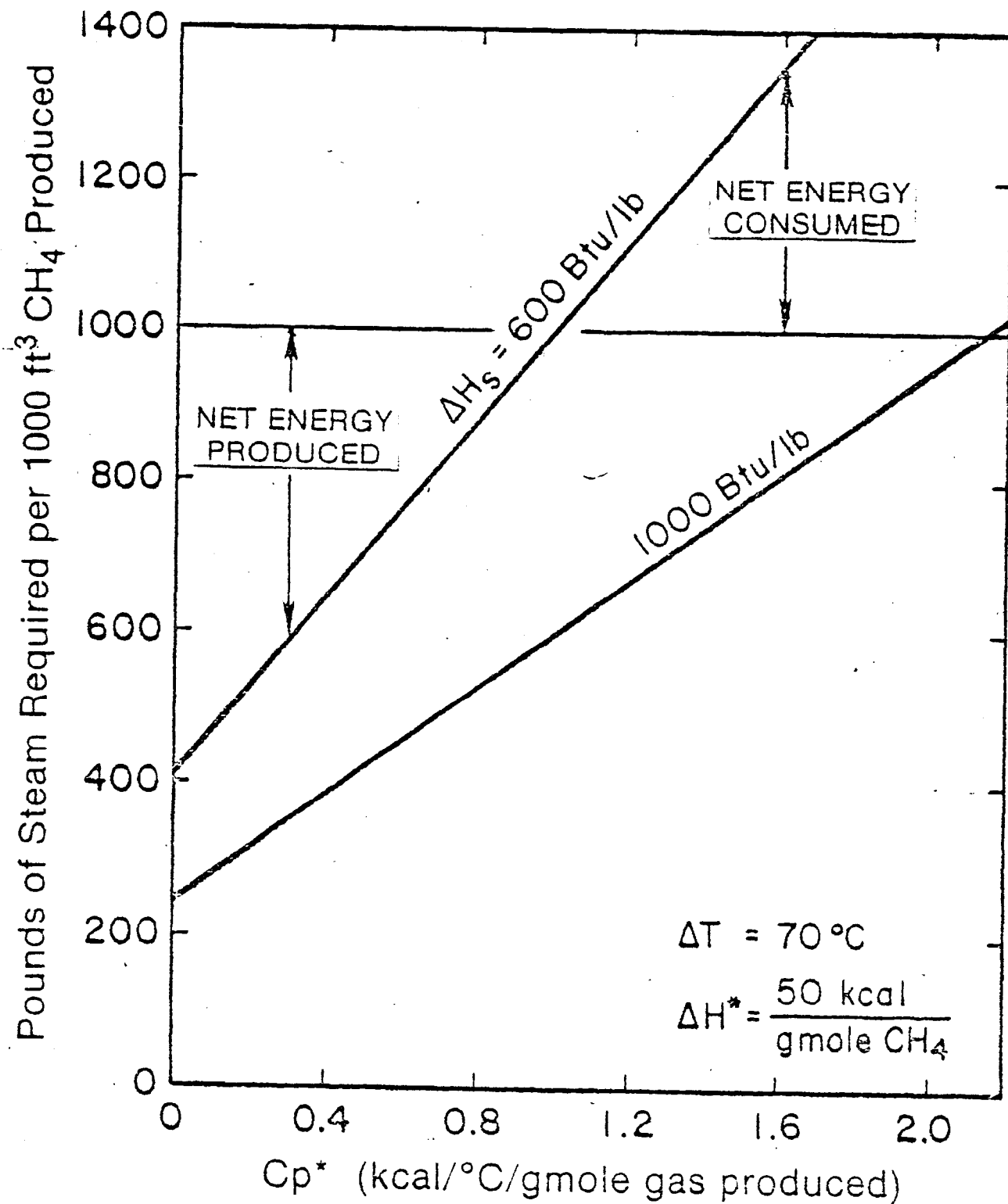


FIGURE 8: The Effect of the Modified Reservoir Heat Capacity on the Amount of Steam Required for Hydrate Dissociation.

the temperature of the reservoir is raised, the sensible heat of the reservoir consumes 3 k cal.

Figure 5 through 8 show how the steam requirement per mole of gas produced varies with latent heat and the reservoir temperature increase. Figure 5 shows the energy input/output ratio, expressed here in lbs of steam/1000 ft<sup>3</sup> of CH<sub>4</sub>, as a function of the combined latent and sensible heats of hydrate dissociation. In this figure the average reservoir temperature increase is assumed to be 30°C. The value of  $\Delta H_g$  is the amount of latent heat of the steam which is used to heat of the reservoir. If  $\Delta H_g$  is 1000 Btu/lb then all of the latent heat is transferred to the reservoir. If  $\Delta H_g$  is 800 or 600 Btu/lb, then 80 percent or 60 percent, of the latent heat of the steam is transferred to the reservoir, respectively. In these two cases, the remaining 20 percent and 40 percent are considered to be heat losses.

Figures 6 and 7 show similar curves for average reservoir temperature increases of 50°C and 70°C respectively. It is unlikely that temperature increases as large as 70°C would be required since hydrates will generally dissociate at temperatures less than 25°C. A 70°C increase would imply that the reservoir temperature was normally (-45°C), which is highly unlikely in any region. However, in order to effect a rapid rate of gas production, some increase above the hydrate

equilibrium dissociation temperature will be required. Therefore, a 70°C increase may, in fact, be desirable.

Figure 8 shows how the input/output energy ratio depends upon the modified reservoir heat capacity,  $C_p^*$ . As Equation (7) shows, this term incorporates  $\phi$ , the fraction of the reservoir containing hydrate, and  $\alpha$ , the fraction of the dissociated gas which is actually produced. It is conceivable that  $C_p^*$  ranges from zero to very high values (20 or more), but is more likely that a typical hydrate reservoir will have a value between 0.1 and 0.5 k cal/°C/g mole CH<sub>4</sub> produced. The upper line in Figure 6, shows a most unfavorable case. Here forty percent of the steam energy is lost, and the hydrate reservoir is heated an average of 70°C. In this case, if  $C_p^*$  is greater than 1.0, the energy consumed will be greater than the heating value of the gas. For more favorable cases, it is likely that a net energy production will be obtained for values of  $C_p^*$  as high as 4.

It is clear from these calculations that production of gas from hydrates depends strongly upon

- the fraction of the reservoir which is actually hydrates
- the efficiency of the thermal-injection (steam injection)
- the latent heat of hydrate dissociation
- the fraction of dissociated gas which is actually produceable.

At this point only estimates can be made for these quantities and the material presented can only point to areas in which research is needed. However, it is clear that if future research finds that the reservoir conditions are favorable then the production of gas from hydrate fields is certainly viable from a thermodynamic viewpoint.

## SUMMARY AND IMPLICATIONS FOR FUTURE RESEARCH

The existence of hydrates within the earth has been clearly established and the possibility of vast quantities of natural gas existing in hydrate form has been suggested by seismic velocities, thermal conductivities, anomalous reflectors, thermodynamic conditions (pressure and temperature) within the earth, and most significantly the evolution of large quantities of gas from cores obtained in likely hydrate containing zones. Additionally, thermodynamic evaluation indicates that hydrates, if they exist in a pure enough state in the earth, have good potential for producing gas with a greater energy content than is needed to break down the hydrates -- hydrates can be a net energy source. Despite the large amount of information obtained to date, there exists a wide gulf between the information available and the information needed to evaluate the potential for hydrates as a natural gas source.

The following categories of research appear to offer the best prospects for a adequate evaluation of the energy potential of hydrates.

- Physical Properties. The measurement of the physical properties of pure hydrates and of hydrate containing cores is essential for the adequate interpretation of seismic information. Physical property measurements should include

thermal conductivities, acoustic wave velocities and electrical resistivities.

- Dissociation of Gas Hydrates. In order to better model the breakdown of hydrates in the earth, the type of heat transfer which occurs during hydrate dissociation should be studied. Heat transfer during a three phase transition has not been studied and so no general method for predicting heat transfer during hydrate dissociation exists.
- Seismic Profiling. Oceanic hydrate resources can be mapped if additional seismic data is obtained. To realistically estimate the quantities of hydrates within the earth more comprehensive seismic profiling is needed. Such data, in conjunction with the physical property measurements will allow good estimates of the depth and areal extent of hydrate fields.
- Coring of Hydrate Fields. Actual pressurized temperature controlled cores should be obtained in regions where hydrates are expected to exist. These cores will provide a direct indication of the quantity of gas available per unit reservoir volume. They also could act as experimental specimens for measuring physical properties. Safety should be a prime consideration in conducting this research.



- Thermodynamic Studies. A greater understanding of hydrate equilibria could be obtained through further thermodynamic studies. One study of importance would be the measurement of methane and other gas concentrations in water which is in equilibrium with hydrates.
- Technology. Studies should be carried out to determine the technology needed for exploitation of hydrate fields since present drilling techniques may be inadequate for production of gas from hydrates. An evaluation of the thermal recovery technique most applicable to hydrate dissociation should also be made.

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September 1979

43

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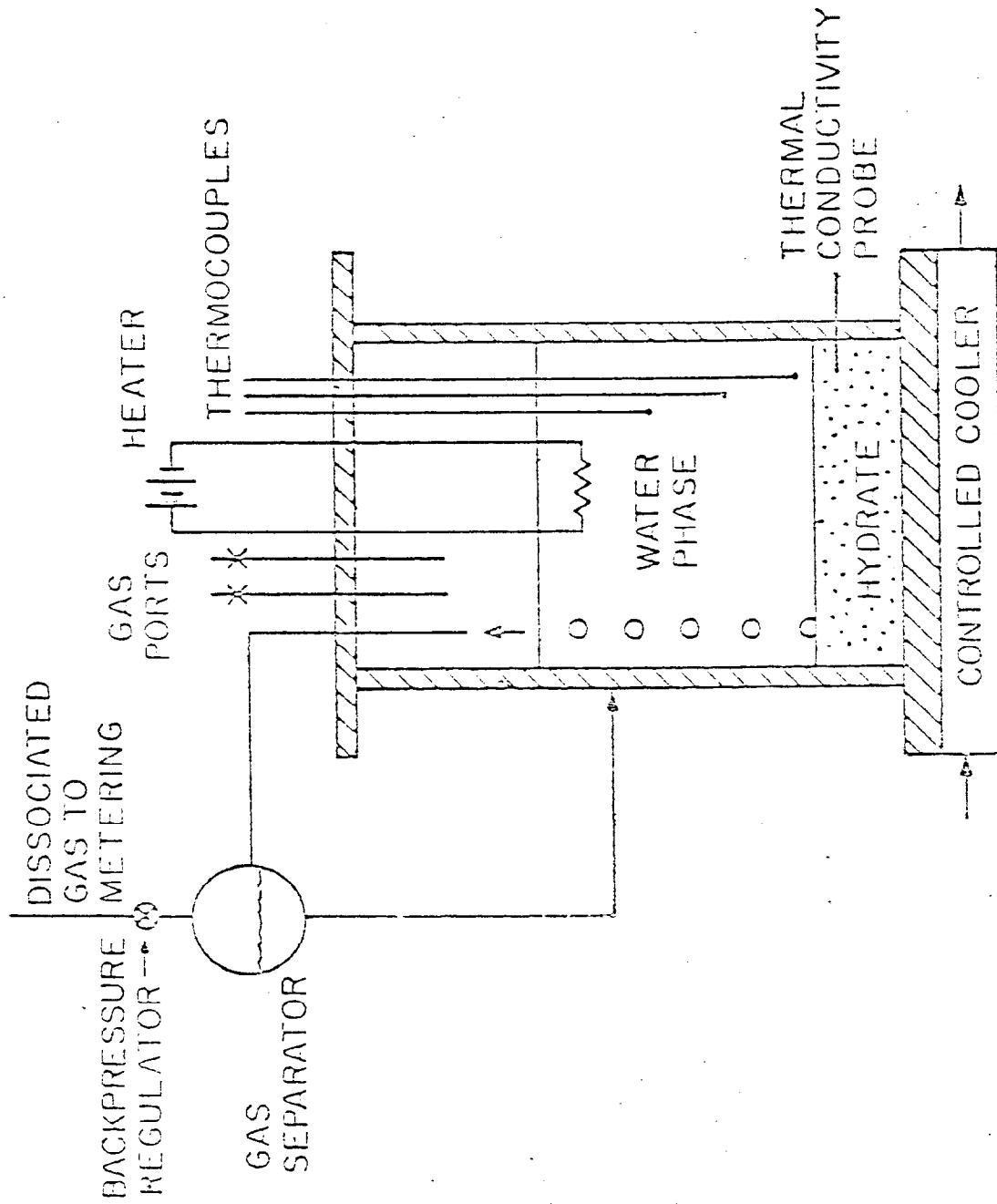
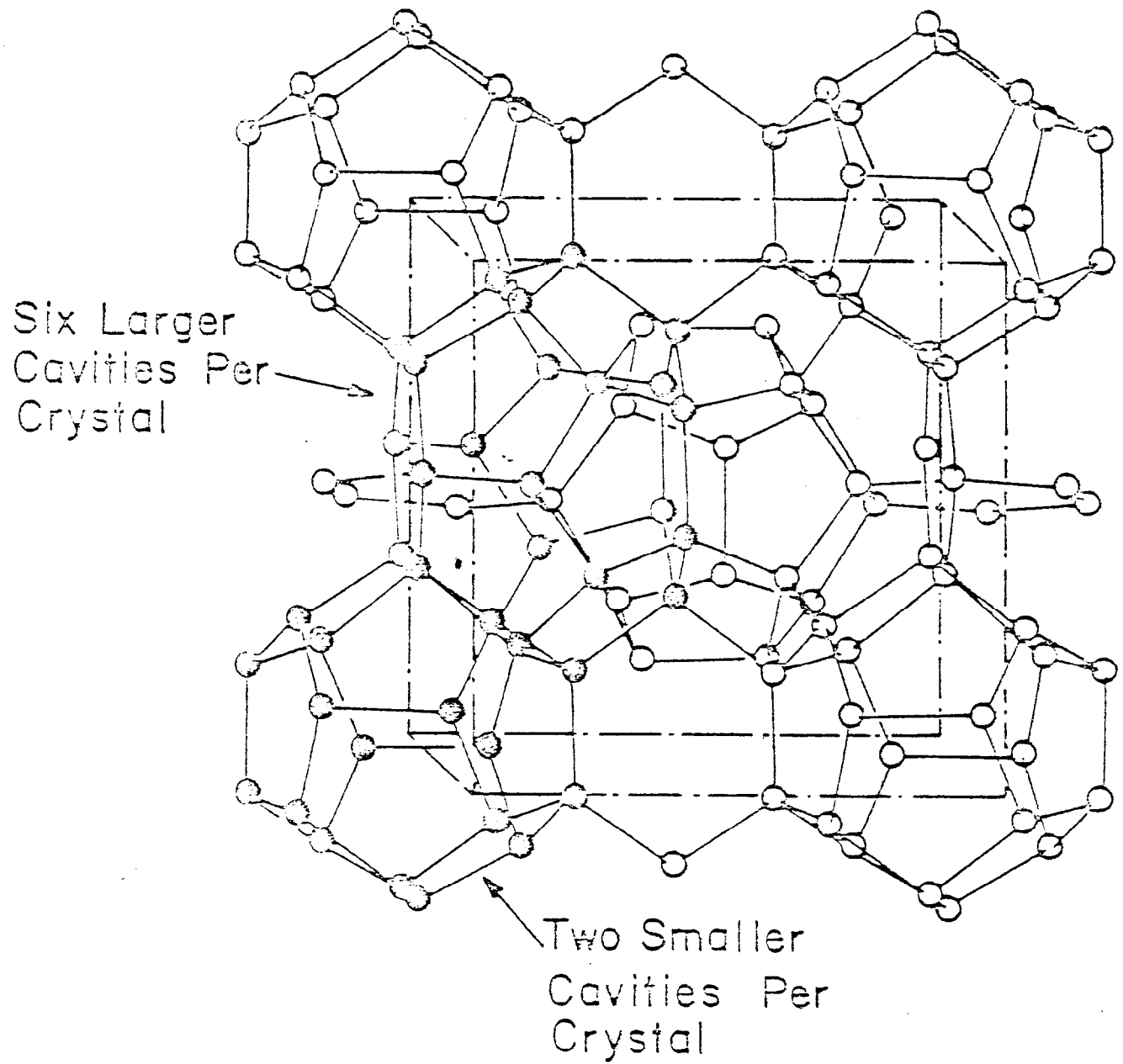
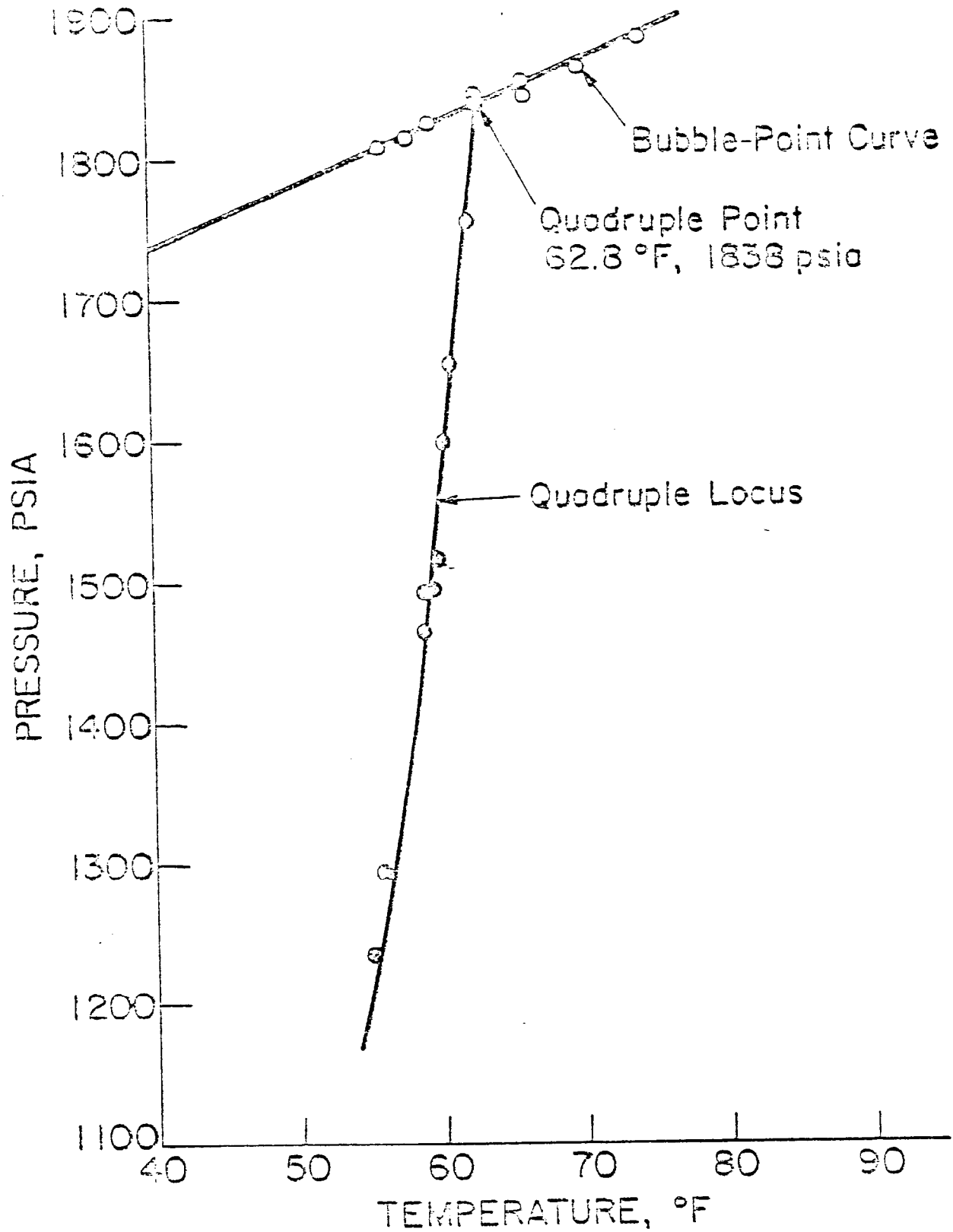


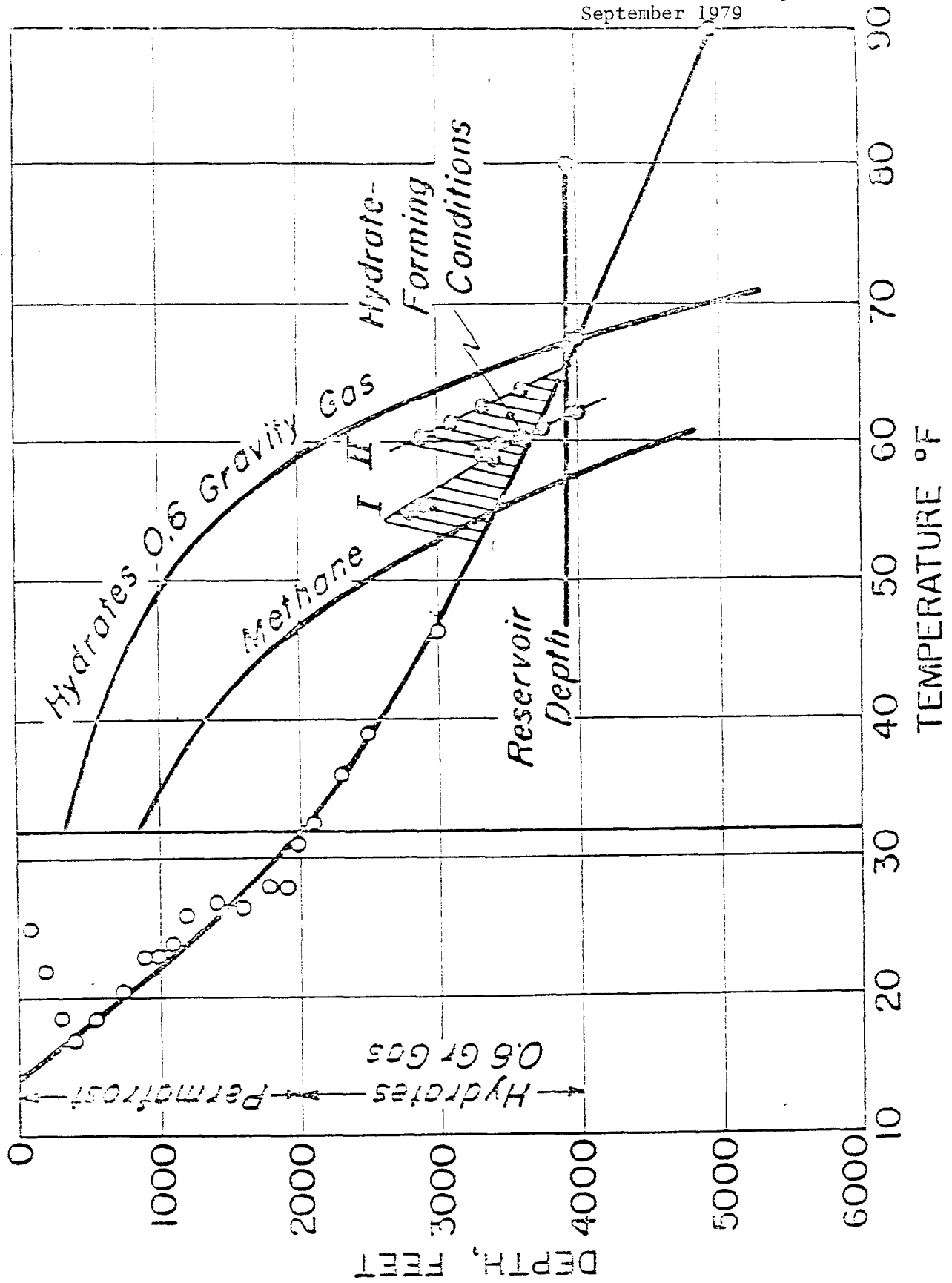
Figure 6 : SCHEMATIC DIAGRAM OF THE EXPERIMENTAL APPARATUS

54









## GOALS OF THE RESEARCH

- MAP REGIONS WHERE HYDRATES MAY EXIST
- DETERMINE THE EXTENT AND PURITY OF HYDRATE FIELDS
  - PRESSURIZED CORE SAMPLE
  - ANALYSIS OF ACOUSTIC DATA
- OBTAIN PHYSICAL PROPERTY DATA INCLUDING THERMAL CONDUCTIVITIES AND AND ELECTRICAL RESISTIVITIES OF HYDRATES
- EXPERIMENTALLY SIMULATE HYDRATE DISSOCIATION AND MEASURE HYDRATE DISSOCIATION HEAT TRANSFER COEFFICIENTS
- DEVELOPE A MATHEMATICAL MODEL OF HYDRATE DISSOCIATION

58

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Univ. of Pittsburgh  
September 1979

| <u>HYDRATE STRUCTURE</u>                |                    |                     |
|---|--------------------|---------------------|
|   | <u>STRUCTURE I</u> | <u>STRUCTURE II</u> |
| NUMBER OF WATER MOLECULES<br>PER CAVITY | 5.75               | 5.67                |
| MAXIMUM PERCENT GAS                     | 17.39              | 17.65               |

57

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# THERMODYNAMIC REQUIREMENTS

|   |                   |
|---|-------------------|
| HEAT OF COMBUSTION OF THE GAS<br>RELEASED FROM THE HYDRATES         | 200-230 KCAL/MOLE |
| LATENT HEAT REQUIRED TO PRODUCE<br>GAS THROUGH HYDRATE DISSOCIATION | 15-30 KCAL/MOLE   |
| NET THERMODYNAMIC ENERGY GAIN                                       | 170-215 KCAL/MOLE |

PRELIMINARY ESTIMATES OF SUB-SURFACE HYDRATE FORMATIONS

- AS MUCH AS  $10^{18}$  CUBIC METERS OF NATURAL GAS MAY EXIST IN THE HYDRATE STATE.
- MUCH OF ALASKA, NORTHERN CANADA AND RUSSIAN SIBERIA HAVE CLIMATES SUITABLE FOR HYDRATE FORMATION AT DEPTHS BETWEEN 300 AND 1500 METERS ( 1000 TO 5000 FEET).
- VIRTUALLY THE ENTIRE OCEAN BOTTOM HAS CONDITIONS SUITABLE FOR HYDRATE FORMATION.

CONDITIONS REQUIRED FOR HYDRATE FORMATION

LOW TEMPERATURES

HIGH PRESSURES

WATER

LIGHT NON-POLAR GAS(ES)